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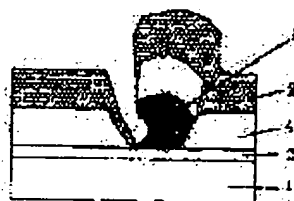
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(54) SUBSTRATE WITH INTERMEDIATE RESISTOR FOR ORGANIC LED ELEMENT, AND ORGANIC LED ELEMENT**(57)Abstract:**

PROBLEM TO BE SOLVED: To provide a substrate for an LED element restrained from short-circuiting, and to obtain an LED element with high reliability.

SOLUTION: By laminating an intermediate resistor film 3 made of a transparent metal oxide of which, the film thickness is 10 nm-10 μ m, the resistance in the direction of film thickness is 0.01-2 Ω per cm², and the ionization energy at the surface of the resistor film is 5.1 eV or more, on the whole or partial of light emission area on a positive electrode or a negative electrode 2 formed into transparent electrode pattern which is formed on a transparent substrate 1 made of glass or resin, short-circuiting is prevented and spread of the defect of the element is prevented, even when a fault is generated on an evaporated film due to the shading caused by a projection or a foreign substance 5 on the surface of the electrode.

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CLAIMS

[Claim(s)]

[Claim 1] It is a some or all top on the luminescence field on the anode plate which consists of a translucency electrode pattern formed on the transparence substrate which consists of glass or resin, or cathode. 10nm - 10 micrometers of thickness, and 1cm² The substrate with the middle resistance film for organic LED components characterized by to carry out the laminating of the middle resistance film with which the ionization energy of 0.01-2ohm, and a resistance film front face consists the electric resistance of the direction of thickness of a hit] of a translucency metallic oxide 5.1eV or more.

[Claim 2] The substrate for organic LED components of claim 1 characterized by consisting of an indium oxide with which the middle resistance film was formed or calcinated by the oxidizing atmosphere as conductive metallic oxide at least.

[Claim 3] The substrate for organic LED components of claim 1 with which the middle resistance film is characterized by the multiple oxide film of conductive metallic oxide and a non-conductive metallic oxide, or being the compound oxidation nitride film of conductive metallic oxide and a non-conductive metal nitride at least at least.

[Claim 4] The substrate for organic LED components of claim 2 characterized by being the multiple oxide film which contains a silicon oxide as an indium oxide and a non-conductive metallic oxide as conductive metallic oxide.

[Claim 5] The organic LED component characterized by having carried out the laminating of an organic luminescence medium layer and the counterelectrode layer to order, and forming them at least on some or all on the luminescence field of the substrate with the middle resistance film of claims 1-4 for organic LED components.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to an organic light emitting diode (LED) component.

[0002]

[Description of the Prior Art] Usually, an organic LED component is formed on transparence substrates, such as a glass plate and a transparence resin film, in order of an anode plate pattern, an organic luminescence medium layer, and a cathode metal layer. As an anode plate, simple substance metal membranes, such as gold of translucency, palladium, platinum, and copper, those alloy film, the cascade screen of a transparence oxide electrode and a metal membrane, or the numerical aperture in a luminescence field is used for 50% or more of the shape of a slit, a mesh-like metal electrode, the spreading electrode of the poly thiophene system conductive polymer, etc. by transparence oxide film, such as ITO (multiple oxide of an indium and tin), and IZO (multiple oxide of an indium and zinc), or 10nm or less of thickness.

[0003] Next, after an organic luminescence medium layer with a thickness of about 100-150nm it is thin from an organic electron hole transportation layer, an organic luminous layer, an organic electron injection layer, etc. is formed by approaches, such as vacuum evaporatio and wet coating, on an anode plate, cathode, such as a MgAg alloy, an AlLi alloy, and aluminum, is vapor-deposited as cathode, and an organic LED component is formed.

[0004] Moreover, cathode can also produce a transparent organic LED component by forming the transparent conductive oxide film after [ITO and IZO] forming a MgAg alloy etc. in translucency 10nm or less.

[0005] In order to reduce the ionization energy of an interface in order to obtain high brightness by the low battery more, and to improve electron injection effectiveness, forming the alkali-metal content layer of Li complex, LiF, Oxidation Li, or Cs between an organic luminescence medium layer and catholyte is also performed.

[0006] Moreover, an organic LED component can also be formed in order of cathode, an organic luminescence medium, and an anode plate on a transparence substrate contrary to usual.

[0007] Since four layers of organic luminescence media between the anode plate on a substrate 1 and the cathode electrode 2 are very thin as a trouble on production of an organic LED component, When a minute projection and the adhesion foreign matter 5 are shown in an anode plate front face, as drawing 3 shows, as for the part of the shade, an organic luminescence medium is not vapor-deposited. When an anode plate and cathode contact directly in the part when a cathode metal is vapor-deposited, or a cavity is generated between anode plate cathode, there is a problem which becomes the cause which destroys a lifting component about leakage current or discharge.

[0008] The point [emitting / un-/ light] centering on the destructive section produces it in order for moisture and oxygen to invade from the hole opened to cathode and to cause oxidation of cathode while the gas which occurred in the destructive section raises a cathode metal layer and makes cathode exfoliate from a luminous layer or an electron injection layer.

[0009] Therefore, an anode plate is wanted not to have the projection of several 10nm or more. Crystal grain grows and the ITO film usually becomes the unevenness whose front face is several 10nm, although an elevated-temperature sputter is carried out and membranes are formed above 200 degrees C for the reduction in resistance. Although surface smoothing by polish was tried, in order to grind the thin film on the glass plate which a polish blemish and an abrasive material tend to remain and has a wave in uniform thickness, the special grinding method by an ionized cluster beam etc. was required for unevenness.

[0010] Moreover, there was also a problem which an etching edge becomes uneven under the effect of crystal grain since the film is polycrystal when carrying out wet etching of the ITO which carried out elevated-temperature membrane formation from an acid and carrying out pattern formation, an organic luminescence medium vacuum evaporation layer becomes thin by the shade, or high electric field are built over a height, and a component tends to short-circuit.

[0011] As an approach of being at the membrane formation time and making it smooth, there is an approach using the amorphous film which is below room temperature extent and formed substrate temperature. ITO in which resistivity carried out elevated-temperature membrane formation although effectiveness was raised to the amorphous ITO film and the IZO film reducing leakage current and a short circuit since the amorphous film had very high surface smooth nature and formed an etching edge in the shape of a taper about twice -- it is not the approach of solution of the short circuit by the high problem and the adhesion foreign matter.

[0012] Although the substrate was treated in the clean room in order to prevent the adhesion foreign matter to a substrate top, it was a very difficult problem that one does not make the dust of about 0.1 micrometer adhere on a large area substrate.

[0013] Although it is also possible to bury the part which heat-treats an electron hole transportation layer more than after [vacuum evaporation] glass transition temperature, was made to carry out a softening flow as an approach of preventing a short circuit, became the shade of an adhesion foreign matter, and was un-vapor-depositing even if an adhesion foreign matter is on a substrate. Usually, the electron hole transportation layer ingredient currently used required time amount for that the expensive electron hole transportation ingredient which it crystallizes with heating, and the film tends to become irregularity, does not crystallize with heating, but has the special, very high molecular structure of amorphous nature is needed, and heating cooling, and the problem was in productivity.

[0014]

[Problem(s) to be Solved by the Invention] This invention is accomplished in view of the above trouble, and it aims at controlling the projection of the electrode surface of an organic LED component, the leakage current by the substrate adhesion foreign matter, and the bad influence of an electric short circuit.

[0015]

[Means for Solving the Problem] This invention the some or all top on the luminescence field on the anode plate which consists of a translucency electrode pattern formed on the transparence substrate which consists of glass or resin, or cathode 10nm - 10 micrometers of namely, thickness, And 1cm² The electric resistance of the direction of thickness of a hit is the substrate with the middle resistance film for organic LED components characterized by carrying out the laminating of the middle resistance film with which the ionization energy of 0.01-20eV, and a resistance film front face consists of a translucency metallic oxide 5.1eV or more. Moreover, it is the substrate for organic LED components of claim 1 characterized by consisting of an indium oxide with which the middle resistance film was formed or calcinated by the oxidizing atmosphere as conductive metallic oxide at least. moreover -- The middle resistance film is the multiple oxide film of conductive metallic oxide and a non-conductive metallic oxide, or the substrate for organic LED components of claim 1 characterized by being the compound oxidation nitride film of conductive metallic oxide and a non-conductive metal nitride at least at least. Moreover, it is the substrate for organic LED components of claim 2 characterized by being the multiple oxide film which contains a silicon oxide as an indium oxide and a non-conductive metallic oxide as conductive metallic oxide.

[0016] Furthermore, this invention is the organic LED component which carried out the laminating of an organic luminescence medium layer and the counterelectrode layer to order at least on the above-mentioned substrate.

[0017]

[Embodiment of the Invention] this invention -- low -- a resistivity transparent electrode -- high -- electrode 2 pattern with which the middle resistance film 3 which has middle resistance of organic luminescence medium 4 resistivity film consists of an anode plate formed on the substrate 1 for organic LED components or cathode is touched, and all the luminescence all [some or] are covered, and the film of one layer is arranged (refer to drawing 1). Or the two-layer film is able to touch the anode plate or cathode pattern formed on the substrate, and each of a counter electrode, and to cover all the luminescence all [some or], and to be arranged (refer to drawing 2).

[0018] It explains in more detail about this invention below. Usually, the volume resistivity of metal electrodes, such as aluminum used for cathode, is 10 to 5 or less ohm-cm, and the volume resistivity of transparent electrodes, such as ITO, is 2×10^4 to 4 or less ohm-cm.

[0019] In the example of the general organic LED component which resistance of a luminescence medium layer becomes from the triphenylamine system electron hole transportation layer whose luminescence medium layer is 50nm, and aluminum oxine complex luminous layer which is 50nm, an organic luminescence medium shows nonlinear resistance, and resistance becomes low, so that applied voltage is high. For example, for organic [LED], although driven by the driver voltage within 10V, the volume resistivity of a defect-free organic luminescence medium layer is usually about 10^6 at 10V of the highest driver voltage in that case. It is an outline 10^6 , even when it is ohm-cm and other luminescence medium ingredients for organic LED are used. It is the resistivity of ohm-cm.

[0020] In that case, resistance of the direction of thickness of a luminescence medium layer is 2 Ω cm. It becomes 10 ohms of hits. then, the electrode material of volume-resistivity 10-5 ohm-cm -- 0.1 supposing it short-circuits inter-electrode by die length of 0.1 micrometers with the area (ten to 10 cm^2) of mum angle and produces a defect -- resistance of a rejected region -- 1ohm per place -- it is -- defect density -- 1 place/ cm^2 it is -- a case -- inter-electrode resistance -- 1 cm^2 per -- it is set to about 0.9 ohms.

[0021] Consequently, area 1 cm^2 In the case of a constant current driver element, there was a problem on which brightness decreases sharply while most currents carried out one half leak by the defective part and applied voltage decreased, when there was an one-place defect. Moreover, in the case of a constant voltage drive component, the current density of a defective part became high and there was a problem which leads to destruction of a component with the Joule's heat.

[0022] Moreover, in an X-Y-matrix display, the cross talk increased by the leakage current from a defective part, and there was a problem to which a display becomes indistinct.

[0023] The middle resistance film of this invention prevents direct contact of the electrodes in the poor vacuum evaporation defective mosquito place of the organic luminescence medium by foreign matter adhesion, a projection, etc. on the front face of a substrate, and since a current leaks through the middle resistance film in the poor vacuum evaporation mosquito place of an organic luminescence medium, leakage current can be sharply controlled compared with the case where electrodes contact directly.

[0024] Since resistance of the middle resistance film starts resistance and the serial of a luminescence medium, in order to make power loss small, 1/5 or less [of the resistance of the direction of thickness of a luminescence medium] is desirable. That is, when driving by the driver voltage not more than 10V, resistance of the organic LED component without the middle resistance film at the time of 10V impression [minimum resistance / of a luminescence medium] is 2 Ω cm. Supposing it is 10ohms of hits, preferably, resistance of the direction of thickness of the middle resistance film is referred to as 0.5 or less ohms, and can control 2ohms or less of aggravation of the current-voltage characteristic of the organic LED component by the increment in resistance at the time of putting in the middle resistance film.

[0025] When the resistance of the resistance film of the direction of thickness is 1/5 or more [of resistance of the direction of thickness of a luminescence medium], if the driver voltage of a component

disregards wiring resistance, while going up by 1.2 or more twice and luminous efficiency's falling, degradation of a component speeds up by the increment in the Joule's heat in a resistive layer.

[0026] Moreover, when carrying out the laminating of the middle resistance film of this invention by solid one on the substrate in which transparent electrode Rhine of an X-Y-matrix display was formed, when the tooth space between transparent electrode Rhine is narrow to several micrometers or less at 1000 or less, the case of the resistance of the direction of thickness of a luminescence medium where it becomes impossible to disregard the leakage current between transparent electrodes, and a cross talk arises has 1/of resistance of the middle resistance film of the direction of thickness.

[0027] In that case, when resistance of the middle resistance film 3 is low, it is desirable to make thickness into thinness, or to dissociate and carry out a laminating for every transparent electrode Rhine like drawing 4.

[0028] The thickness of the middle resistance film of the substrate for organic LED components of this invention is formed by the thickness of 10nm - 10 micrometers. When the thickness of the middle resistance film is the same about 100nm as a luminescence medium layer, it is a volume resistivity 104-105. It is desirable to use the resistance film of omega-cm extent.

[0029] When the middle resistance film is set to 10nm or less, the irregularity or the adhesion foreign matter of an electrode surface may fully be unable to be covered.

[0030] When the middle resistance film is formed in 10 micrometers or more, the leakage current between the problem of film peeling by membrane stress or a crack, the problem whose membrane formation cost increases, anode plate inter-electrode, or the anode plate which has not been chosen and cathode increases, and it is easy to produce a blot and cross talk of luminescence.
 [0031] When carrying out the laminating of the middle resistance film on a translucency anode plate and taking out light from an anode plate side, also as for the middle resistance film, it is desirable to penetrate an emission spectrum organic [LED] as much as possible. By this invention, an energy gap uses a metallic-oxide ingredient as an ingredient in which it is large and 50% or more light transmission is possible in a light field.

[0032] The resistivity of the ingredient known as a transparence electric conduction film ingredient as a metallic-oxide ingredient used for the middle resistance film can be raised and used.

[0033] As an example of the ingredient known as a transparence electric conduction film ingredient, the metaled oxygen deficiency mold transparent conductive oxide or metaled multiple oxide chosen from Mg, Zn, Ga, germanium, In, and Sn at least one or more is raised. concrete -- In 2O3, In2-X GaX O3, ITO, IZO and SnO2, Sn1-X GeX O2, ZnO, and ZnX Mg1- XO and AgInO2 etc. -- it is.

[0034] Moreover, the metaled hyperoxia mold transparent conductive metallic oxide or metaled multiple oxide chosen from Sr, nickel, Cu, and aluminum at least one or more is raised. concrete -- NiO, CuAlO2, and SrCu 2O2 etc. -- it is.

[0035] as the approach of raising the resistivity of these film -- the case of an oxygen deficiency mold transparent conductive metallic oxide or a multiple oxide -- usually -- low -- it is reducing an oxygen deficiency and reducing a carrier consistency by raising the oxygen density of a membrane formation ambient atmosphere, forming membranes rather than the conditions which form the oxide film [****] by reactive deposition or the spatter, and reducing the oxygen deficiency in the film, or heat-treating by the oxidizing atmosphere after membrane formation. Or also by doping univalent metal, such as Li, Cu, etc. which crush an oxygen defect, conductivity can be reduced and it can raise to suitable resistance.

[0036] the case of a hyperoxia mold transparent conductive metallic oxide or a multiple oxide -- reverse -- usually -- low -- it is reducing the oxygen density at the time of membrane formation rather than the conditions which form the oxide film [****], or calcinating in a membrane formation post reduction ambient atmosphere.

[0037] At the time of membrane formation, the film may be a metal membrane or an imperfect metallic oxide, and after membrane formation, in the case of the hyperoxia mold transparent conductive metallic oxide or multiple oxide containing In, it processes at 150 degrees C - 400 degrees C in oxidizing atmospheres, such as oxygen and an ozone ambient atmosphere, it advances oxidation, and can also form the oxide film. However, heat treatment advances crystallization of the middle resistance film, and

may be formed into low resistance rather than desired resistance by improvement in mobility accompanying crystallization.

[0038] As an approach of raising other resistivity, in conductive metallic oxide, moreover, SiO₂ with high resistivity, aluminum 2O₃, GeO₂, and Ta 2O₅, Y₂ O₃ etc. -- a non-conductive metallic oxide or Si₃ N₄ etc. -- it is mixing a non-conductive metal nitride at 1 / about ten to 10/1 suitable rate by (the metal atomic number in a non-conductive metallic oxide or a nitride) / (metal atomic number in conductive metallic oxide) ratio, and compounding.

[0039] Using the evaporation material or target ingredient which compounded beforehand those configuration metals or the metallic oxide, and the metal nitride, from a separate evaporation source or a separate target, oxygen and the bottom reactive deposition of nitrogen-gas-atmosphere kind, pulse laser deposition, a sputter, etc. are performed to coincidence, and the method of compounding conductive metallic oxide, a non-conductive metallic oxide, or a nitride can be formed.

[0040] Into the target of the oxidation In which is conductive metallic oxide, or ITO, it mixes beforehand and, specifically, the sputter of the silicon nitride which are an aluminum oxide or non-conductive metal nitrides, such as silicon oxides, such as a silica which is a non-conductive metallic oxide, and an alumina, is carried out. Or vapor codeposition of the SiO is carried out to coincidence, carrying out reactive deposition of the In in an oxygen ambient atmosphere. Or after carrying out vapor codeposition of In and the SiO, the middle resistance film is producible by the approach of calcinating in an oxygen ambient atmosphere.

[0041] For example, if vapor codeposition of the SiO is carried out for Oxidation In during a sputter in an oxygen ambient atmosphere at a rate of about 10 - 200% of metal atomic ratios and membranes are formed at a substrate temperature room temperature, even when the high film of smooth amorphous nature can be formed and is heated at about 300 degrees C, the non-conductive silicon oxide in the film can bar crystallization of the conductive oxidation In, low resistance-ization by the improvement in mobility accompanying crystallization can be controlled, and thermal stability will increase.

[0042] Moreover, in the substrate for organic LED components with the middle resistance film, in order for the middle resistance film to make an electron hole easy to inject into an organic luminescence medium layer, the front face needs to have big ionization energy equivalent to the electron hole transportation ingredient which constitutes an organic luminescence medium.

[0043] The copper phthalocyanine and triphenylamine system electron hole transportation ingredient which are generally used for organic [LED] are measured by Riken Keiki tabulation side analysis apparatus AC-1. 5.1 to 5.8 eV, Since aluminum oxine complex of luminescent material has the ionization energy of about 5.8eV, in order to carry out a hole injection to the organic luminescence medium of an electron hole transportation layer or a luminous layer efficiently by low driver voltage, at least 5.1eV or more of ionization energy of about 5.8eV is called for preferably.

[0044] since a carrier consistency also falls by forming the transparence oxide electric conduction film and a silicon oxide into 10-200 atom % extent compound to metal atoms other than silicon in this invention -- usually -- low -- the ionization energy 5.5eV or more with bigger ITO used as a transparent electrode [****] than 4.8eV is also realizable.

[0045]

[Example] <an example 1> -- first -- taper etching (18 components of 2x3mm of light-emitting parts) of the distance of an ITO target (tin oxide 10wt%) with a diameter of 5 inches and a jig side was carried out to the shape of a stripe by the organic acid after room temperature membrane formation in 17.5cm and an argon ambient atmosphere (pressure of 0.34Pa) by RF magnetron sputtering (TOKUDA CFS-10EP-70) RF output 300W. Next, it annealed among 1-hour air at 300 degrees C, and the substrate with an ITO electrode pattern (20ohm/ **) (5cm angle) of 190nm of thickness was produced.

[0046] Next, carrying out the sputter of the ITO to a 3 inch RF magnetron SUPPATA ring gun by RF output 250 W using vacuum membrane formation equipment with the source of resistance heating vacuum evaporation by the argon / oxygen = 10 / 1 (pressure of 0.34Pa), the resistance heating vacuum evaporation of the SiO was carried out, the laminating of the middle resistance film was carried out by solid one by the thickness of 1 micrometer on the ITO electrode pattern, and the substrate with the

middle resistance film was produced. The obtained film was transparent and amorphous at X diffraction measurement. Si / (In+Sn) surface ratio = About 25 atoms % and a volume resistivity are 7×10^3 . They were $\Omega\text{-cm}$ and 5.5eV of ionization energy.

[0047] On the substrate with the middle resistance film produced in the <example 2> example 1, they are N, N'-diphenyl-N, and N' as an electron hole transportation layer. -(1-naphthyl)- A benzidine 50nm, After vapor-depositing 50nm for aluminum oxine complex in order as a luminous layer and carrying out 0.5nm vapor codeposition of the LiF as cathode, 200nm laminating of the aluminum was carried out, and 18 elements were produced for the organic LED component (light-emitting part $2 \times 3 \text{mm}^2$) on the substrate. In addition, the component was produced all over the clean booth of a class 1000.

[0048] All the 18 elements that produced this component measured resistance between terminals including wiring resistance with the circuit tester (about 1.7V impression), and there was no short circuit with the resistance more than 30 M Ω (upper limit of circuit tester measurement). All components are 5000-hour or more 500 cd/m² at the electrical potential difference not more than 7V. Light is emitted to stability by the above brightness.

[0049] The component was produced like the example 2 using the ITO substrate (4.8eV of surface ionization energy) without the <example 1 of comparison> middle resistance film.

[0050] Consequently, during 18-piece production, 15 elements were measured with the circuit tester (about 1.7V impression), there is a component one element and whose 200Kohm 30 M Ω or more and 11 M Ω are one element and 1 Kohm, and the short-circuited component produced them. The component with 30-M Ω or more resistance emits light to stability by the driver voltage not more than 7V for 5000 hours or more, within 1000 hours, the point emitting [un-] light would carry out breadth short-circuit, and the component not more than 200Kohm will not shine. The current potential property was formed into 1-2V high voltage rather than the component produced in the example 2.

[0051] <Example 3> First the distance of an ITO target (tin oxide 10wt%) with a diameter of 5 inches and a jig side by RF magnetron sputtering (TOKUDA CFS-10EP-70) 17.5cm, In an argon ambient atmosphere (pressure of 0.34Pa) RF output 300W After room temperature membrane formation, Taper etching (18 components of $2 \times 3 \text{mm}$ of light-emitting parts) was carried out to the shape of a stripe by the organic acid, it annealed among 1-hour air at 300 degrees C, and the substrate with an ITO electrode pattern (20ohm/ **) (5cm angle) of 190nm of thickness was produced.

[0052] Next, carrying out the spatter of the indium oxide to a 3 inch RF magnetron SUPPATA ring gun by RF output 250 W using vacuum membrane formation equipment with the source of resistance heating vacuum evaporation by the argon / oxygen = 10 / 1 (pressure of 0.34Pa), the resistance heating vacuum evaporation of the SiO was carried out, and the laminating of the middle resistance film was carried out to coincidence by solid one by the thickness of 1 micrometer on the ITO electrode pattern. Then, it heat-treated at 300 degrees C among air, and the substrate with the middle resistance film was produced. The obtained film was transparent and amorphous at X diffraction measurement. Surface Si/In ratio = About 125 atoms % and a volume resistivity were 100 ohm-cm and 5.6eV of ionization energy.

[0053] 18 elements were produced like the example 2 on the substrate with the middle resistance film obtained in the <example 4> example 3.

[0054] Consequently, as for this component, the short circuit did not have 18 pieces with the resistance more than 30 M Ω (it measures by 3V). All components are 5000-hour or more 500 cd/m². Light is emitted to stability by the above brightness.

[0055]

[Effect of the Invention] By the above, the substrate with the middle resistance film by this invention can control the projection of the electrode surface of an organic LED component, the leakage current by the substrate adhesion foreign matter, and the bad influence of an electric short circuit so that clearly. Therefore, when it considers as an organic LED component, effectiveness is in defective expansion prevention and reinforcement.

[0056]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to an organic light emitting diode (LED) component.

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PRIOR ART

[Description of the Prior Art] Usually, an organic LED component is formed on transparence substrates, such as a glass plate and a transparence resin film, in order of an anode plate pattern, an organic luminescence medium layer, and a cathode metal layer. As an anode plate, simple substance metal membranes, such as gold of translucency, palladium, platinum, and copper, those alloy film, the cascade screen of a transparence oxide electrode and a metal membrane, or the numerical aperture in a luminescence field is used for 50% or more of the shape of a slit, a mesh-like metal electrode, the spreading electrode of the poly thiophene system conductive polymer, etc. by transparence oxide film, such as ITO (multiple oxide of an indium and tin), and IZO (multiple oxide of an indium and zinc), or 10nm or less of thickness.

[0003] Next, after an organic luminescence medium layer with a thickness of about 100-150nm it is thin from an organic electron hole transportation layer, an organic luminous layer, an organic electron injection layer, etc. is formed by approaches, such as vacuum evaporatio~~no~~ and wet coating, on an anode plate, cathode, such as a MgAg alloy, an AlLi alloy, and aluminum, is vapor-deposited as cathode, and an organic LED component is formed.

[0004] Moreover, cathode can also produce a transparent organic LED component by forming the transparent conductive oxide film after [ITO and IZO] forming a MgAg alloy etc. in translucency 10nm or less.

[0005] In order to reduce the ionization energy of an interface in order to obtain high brightness by the low battery more, and to improve electron injection effectiveness, forming the alkali-metal content layer of Li complex, LiF, Oxidation Li, or Cs between an organic luminescence medium layer and catholyte is also performed.

[0006] Moreover, an organic LED component can also be formed in order of cathode, an organic luminescence medium, and an anode plate on a transparence substrate contrary to usual.

[0007] Since four layers of organic luminescence media between the anode plate on a substrate 1 and the cathode electrode 2 are very thin as a trouble on production of an organic LED component, When a minute projection and the adhesion foreign matter 5 are shown in an anode plate front face, as drawing 3 shows, as for the part of the shade, an organic luminescence medium is not vapor-deposited. When an anode plate and cathode contact directly in the part when a cathode metal is vapor-deposited, or a cavity is generated between anode plate cathode, there is a problem which becomes the cause which destroys a lifting component about leakage current or discharge.

[0008] The point [emitting / un-/ light] centering on the destructive section produces it in order for moisture and oxygen to invade from the hole opened to cathode and to cause oxidation of cathode while the gas which occurred in the destructive section raises a cathode metal layer and makes cathode exfoliate from a luminous layer or an electron injection layer.

[0009] Therefore, an anode plate is wanted not to have the projection of several 10nm or more. Crystal grain grows and the ITO film usually becomes the unevenness whose front face is several 10nm, although an elevated-temperature spatter is carried out and membranes are formed above 200 degrees C for the reduction in resistance. Although surface smoothing by polish was tried, in order to grind the thin

film on the glass plate which a polish blemish and an abrasive material tend to remain and has a wave in uniform thickness, the special grinding method by an ionized cluster beam etc. was required for unevenness.

[0010] Moreover, there was also a problem which an etching edge becomes uneven under the effect of crystal grain since the film is polycrystal when carrying out wet etching of the ITO which carried out elevated-temperature membrane formation from an acid and carrying out pattern formation, an organic luminescence medium vacuum evaporation layer becomes thin by the shade, or high electric field are built over a height, and a component tends to short-circuit.

[0011] As an approach of being at the membrane formation time and making it smooth, there is an approach using the amorphous film which is below room temperature extent and formed substrate temperature. 1.5 of ITO in which resistivity carried out elevated-temperature membrane formation although effectiveness was raised to the amorphous ITO film and the IZO film reducing leakage current and a short circuit since the amorphous film had very high surface smooth nature and formed an etching edge in the shape of a taper about twice -- it is not the approach of solution of the short circuit by the high problem and the adhesion foreign matter.

[0012] Although the substrate was treated in the clean room in order to prevent the adhesion foreign matter to a substrate top, it was a very difficult problem that one does not make the dust of about 0.1 micrometer adhere on a large area substrate.

[0013] Although it is also possible to bury the part which heat-treats an electron hole transportation layer more than after [vacuum evaporation] glass transition temperature, was made to carry out a softening flow as an approach of preventing a short circuit, became the shade of an adhesion foreign matter, and was un-vapor-depositing even if an adhesion foreign matter is on a substrate. Usually, the electron hole transportation layer ingredient currently used required time amount for that the expensive electron hole transportation ingredient which it crystallizes with heating, and the film tends to become irregularity, does not crystallize with heating, but has the special, very high molecular structure of amorphous nature is needed, and heating cooling, and the problem was in productivity.

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EFFECT OF THE INVENTION

[Effect of the Invention] By the above, the substrate with the middle resistance film by this invention can control the projection of the electrode surface of an organic LED component, the leakage current by the substrate adhesion foreign matter, and the bad influence of an electric short circuit so that clearly. Therefore, when it considers as an organic LED component, effectiveness is in defective expansion prevention and reinforcement.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention is accomplished in view of the above trouble, and it aims at controlling the projection of the electrode surface of an organic LED component, the leakage current by the substrate adhesion foreign matter, and the bad influence of an electric short circuit.

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MEANS

[Means for Solving the Problem] This invention the some or all top on the luminescence field on the anode plate which consists of a translucency electrode pattern formed on the transparence substrate which consists of glass or resin, or cathode 10nm - 10 micrometers of namely, thickness, And 1cm² The electric resistance of the direction of thickness of a hit is the substrate with the middle resistance film for organic LED components characterized by carrying out the laminating of the middle resistance film with which the ionization energy of 0.01-2ohm, and a resistance film front face consists of a translucency metallic oxide 5.1eV or more. Moreover, it is the substrate for organic LED components of claim 1 characterized by consisting of an indium oxide with which the middle resistance film was formed or calcinated by the oxidizing atmosphere as conductive metallic oxide at least. moreover -- The middle resistance film is the multiple oxide film of conductive metallic oxide and a non-conductive metallic oxide, or the substrate for organic LED components of claim 1 characterized by being the compound oxidation nitride film of conductive metallic oxide and a non-conductive metal nitride at least at least. Moreover, it is the substrate for organic LED components of claim 2 characterized by being the multiple oxide film which contains a silicon oxide as an indium oxide and a non-conductive metallic oxide as conductive metallic oxide.

[0016] Furthermore, this invention is the organic LED component which carried out the laminating of an organic luminescence medium layer and the counterelectrode layer to order at least on the above-mentioned substrate.

[0017]

[Embodiment of the Invention] this invention -- low -- a resistivity transparent electrode -- high -- electrode 2 pattern with which the middle resistance film 3 which has middle resistance of organic luminescence medium 4 resistivity film consists of an anode plate formed on the substrate 1 for organic LED components or cathode is touched, and all the luminescence all [some or] are covered, and the film of one layer is arranged (refer to drawing 1). Or the two-layer film is able to touch the anode plate or cathode pattern formed on the substrate, and each of a counter electrode, and to cover all the luminescence all [some or], and to be arranged (refer to drawing 2).

[0018] It explains in more detail about this invention below. Usually, the volume resistivity of metal electrodes, such as aluminum used for cathode, is 10 to 5 or less ohm-cm, and the volume resistivity of transparent electrodes, such as ITO, is 2x10 to 4 or less ohm-cm.

[0019] In the example of the general organic LED component which resistance of a luminescence medium layer becomes from the triphenylamine system electron hole transportation layer whose luminescence medium layer is 50nm, and aluminum oxine complex luminous layer which is 50nm, an organic luminescence medium shows nonlinear resistance, and resistance becomes low, so that applied voltage is high. For example, for organic [LED], although driven by the driver voltage within 10V, the volume resistivity of a defect-free organic luminescence medium layer is usually about 10⁶ at 10V of the highest driver voltage in that case. It is an outline 10⁶, even when it is omega-cm and other luminescence medium ingredients for organic LED are used. It is the resistivity of omega-cm.

[0020] In that case, resistance of the direction of thickness of a luminescence medium layer is 2 1cm. It

becomes 10 ohms of hits. then, the electrode material of volume-resistivity 10-5 ohm-cm -- 0.1 supposing it short-circuits inter-electrode by die length of 0.1 micrometers with the area (ten to 10 cm²) of mum angle and produces a defect -- resistance of a rejected region -- 1ohm per place -- it is -- defect density -- 1 place/cm² it is -- a case -- inter-electrode resistance -- 1cm² per -- it is set to about 0.9 ohms.

[0021] Consequently, area 1cm² In the case of a constant current driver element, there was a problem on which brightness decreases sharply while most currents carried out one half leak by the defective part and applied voltage decreased, when there was an one-place defect. Moreover, in the case of a constant voltage drive component, the current density of a defective part became high and there was a problem which leads to destruction of a component with the Joule's heat.

[0022] Moreover, in an X-Y-matrix display, the cross talk increased by the leakage current from a defective part, and there was a problem to which a display becomes indistinct.

[0023] The middle resistance film of this invention prevents direct contact of the electrodes in the poor vacuum evaporationno defective mosquito place of the organic luminescence medium by foreign matter adhesion, a projection, etc. on the front face of a substrate, and since a current leaks through the middle resistance film in the poor vacuum evaporationno mosquito place of an organic luminescence medium, leakage current can be sharply controlled compared with the case where electrodes contact directly.

[0024] Since resistance of the middle resistance film starts resistance and the serial of a luminescence medium, in order to make power loss small, 1/5 or less [of the resistance of the direction of thickness of a luminescence medium] is desirable. That is, when driving by the driver voltage not more than 10V, resistance of the organic LED component without the middle resistance film at the time of 10V impression [minimum resistance / of a luminescence medium] is 2 1 cm. Supposing it is 10ohms of hits, preferably, resistance of the direction of thickness of the middle resistance film is referred to as 0.5 or less ohms, and can control 2ohms or less of aggravation of the current-voltage characteristic of the organic LED component by the increment in resistance at the time of putting in the middle resistance film.

[0025] When the resistance of the resistance film of the direction of thickness is 1/5 or more [of resistance of the direction of thickness of a luminescence medium], if the driver voltage of a component disregards wiring resistance, while going up by 1.2 or more twice and luminous efficiency's falling, degradation of a component speeds up by the increment in the Joule's heat in a resistive layer.

[0026] Moreover, when carrying out the laminating of the middle resistance film of this invention by solid one on the substrate in which transparent electrode Rhine of an X-Y-matrix display was formed, when the tooth space between transparent electrode Rhine is narrow to several micrometers or less at 1000 or less, the case of the resistance of the direction of thickness of a luminescence medium where it becomes impossible to disregard the leakage current between transparent electrodes, and a cross talk arises has 1/of resistance of the middle resistance film of the direction of thickness.

[0027] In that case, when resistance of the middle resistance film 3 is low, it is desirable to make thickness into thinness, or to dissociate and carry out a laminating for every transparent electrode Rhine like drawing 4 .

[0028] The thickness of the middle resistance film of the substrate for organic LED components of this invention is formed by the thickness of 10nm - 10 micrometers. When the thickness of the middle resistance film is the same about 100nm as a luminescence medium layer, it is a volume resistivity 10⁴-10⁵. It is desirable to use the resistance film of omega-cm extent.

[0029] When the middle resistance film is set to 10nm or less, the irregularity or the adhesion foreign matter of an electrode surface may fully be unable to be covered.

[0030] When the middle resistance film is formed in 10 micrometers or more, the leakage current between the problem of film peeling by membrane stress or a crack, the problem whose membrane formation cost increases, anode plate inter-electrode, or the anode plate which has not been chosen and cathode increases, and it is easy to produce a blot and cross talk of luminescence.

[0031] When carrying out the laminating of the middle resistance film on a translucency anode plate and taking out light from an anode plate side, also as for the middle resistance film, it is desirable to

penetrate an emission spectrum organic [LED] as much as possible. By this invention, an energy gap uses a metallic-oxide ingredient as an ingredient in which it is large and 50% or more light transmission is possible in a light field.

[0032] The resistivity of the ingredient known as a transparence electric conduction film ingredient as a metallic-oxide ingredient used for the middle resistance film can be raised and used.

[0033] As an example of the ingredient known as a transparence electric conduction film ingredient, the metaled oxygen deficiency mold transparent conductive oxide or metaled multiple oxide chosen from Mg, Zn, Ga, germanium, In, and Sn at least one or more is raised. concrete -- In $2O_3$, $In_2-X GaX O_3$, ITO, IZO and SnO_2 , $Sn_{1-X} GeX O_2$, ZnO, and $ZnX Mg_{1-X} O$ and $AgInO_2$ etc. -- it is.

[0034] Moreover, the metaled hyperoxia mold transparent conductive metallic oxide or metaled multiple oxide chosen from Sr, nickel, Cu, and aluminum at least one or more is raised. concrete -- NiO , $CuAlO_2$, and $SrCu_2O_2$ etc. -- it is.

[0035] as the approach of raising the resistivity of these film -- the case of an oxygen deficiency mold transparent conductive metallic oxide or a multiple oxide -- usually -- low -- it is reducing an oxygen deficiency and reducing a carrier consistency by raising the oxygen density of a membrane formation ambient atmosphere, forming membranes rather than the conditions which form the oxide film [****] by reactive deposition or the spatter, and reducing the oxygen deficiency in the film, or heat-treating by the oxidizing atmosphere after membrane formation. Or also by doping univalent metal, such as Li, Cu, etc. which crush an oxygen defect, conductivity can be reduced and it can raise to suitable resistance.

[0036] the case of a hyperoxia mold transparent conductive metallic oxide or a multiple oxide -- reverse -- usually -- low -- it is reducing the oxygen density at the time of membrane formation rather than the conditions which form the oxide film [****], or calcinating in a membrane formation post reduction ambient atmosphere.

[0037] At the time of membrane formation, the film may be a metal membrane or an imperfect metallic oxide, and after membrane formation, in the case of the hyperoxia mold transparent conductive metallic oxide or multiple oxide containing In, it processes at 150 degrees C - 400 degrees C in oxidizing atmospheres, such as oxygen and an ozone ambient atmosphere, it advances oxidation, and can also form the oxide film. However, heat treatment advances crystallization of the middle resistance film, and may be formed into low resistance rather than desired resistance by improvement in mobility accompanying crystallization.

[0038] As an approach of raising other resistivity, in conductive metallic oxide, moreover, SiO_2 with high resistivity, aluminum $2O_3$, GeO_2 , and Ta_2O_5 , Y_2O_3 etc. -- a non-conductive metallic oxide or Si_3N_4 etc. -- it is mixing a non-conductive metal nitride at 1 / about ten to 10/1 suitable rate by (the metal atomic number in a non-conductive metallic oxide or a nitride) / (metal atomic number in conductive metallic oxide) ratio, and compounding.

[0039] Using the evaporation material or target ingredient which compounded beforehand those configuration metals or the metallic oxide, and the metal nitride, from a separate evaporation source or a separate target, oxygen and the bottom reactive deposition of nitrogen-gas-atmosphere mind, pulse laser deposition, a spatter, etc. are performed to coincidence, and the method of compounding conductive metallic oxide, a non-conductive metallic oxide, or a nitride can be formed.

[0040] Into the target of the oxidation In which is conductive metallic oxide, or ITO, it mixes beforehand and, specifically, the spatter of the silicon nitride which are an aluminum oxide or non-conductive metal nitrides, such as silicon oxides, such as a silica which is a non-conductive metallic oxide, and an alumina, is carried out. Or vapor codeposition of the SiO is carried out to coincidence, carrying out reactive deposition of the In in an oxygen ambient atmosphere. Or after carrying out vapor codeposition of In and the SiO , the middle resistance film is producible by the approach of calcinating in an oxygen ambient atmosphere.

[0041] For example, if vapor codeposition of the SiO is carried out for Oxidation In during a spatter in an oxygen ambient atmosphere at a rate of about 10 - 200% of metal atomic ratios and membranes are formed at a substrate temperature room temperature, even when the high film of smooth amorphous nature can be formed and is heated at about 300 degrees C, the non-conductive silicon oxide in the film

can bar crystallization of the conductive oxidation In, low resistance-ization by the improvement in mobility accompanying crystallization can be controlled, and thermal stability will increase.

[0042] Moreover, in the substrate for organic LED components with the middle resistance film, in order for the middle resistance film to make an electron hole easy to inject into an organic luminescence medium layer, the front face needs to have big ionization energy equivalent to the electron hole transportation ingredient which constitutes an organic luminescence medium.

[0043] The copper phthalocyanine and triphenylamine system electron hole transportation ingredient which are generally used for organic [LED] are measured by Riken Keiki tabulation side analysis apparatus AC-1. 5.1 to 5.8 eV, Since aluminum oxine complex of luminescent material has the ionization energy of about 5.8eV, in order to carry out a hole injection to the organic luminescence medium of an electron hole transportation layer or a luminous layer efficiently by low driver voltage, at least 5.1eV or more of ionization energy of about 5.8eV is called for preferably.

[0044] since a carrier consistency also falls by forming the transparence oxide electric conduction film and a silicon oxide into 10-200 atom % extent compound to metal atoms other than silicon in this invention -- usually -- low -- the ionization energy 5.5eV or more with bigger ITO used as a transparent electrode [****] than 4.8eV is also realizable.

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EXAMPLE

[Example] <an example 1> -- first -- taper etching (18 components of 2x3mm of light-emitting parts) of the distance of an ITO target (tin oxide 10wt%) with a diameter of 5 inches and a jig side was carried out to the shape of a stripe by the organic acid after room temperature membrane formation in 17.5cm and an argon ambient atmosphere (pressure of 0.34Pa) by RF magnetron sputtering (TOKUDA CFS-10EP-70) RF output 300W. Next, it annealed among 1-hour air at 300 degrees C, and the substrate with an ITO electrode pattern (20ohm/ **) (5cm angle) of 190nm of thickness was produced.

[0046] Next, carrying out the spatter of the ITO to a 3 inch RF magnetron SUPPATA ring gun by RF output 250 W using vacuum membrane formation equipment with the source of resistance heating vacuum evaporation by the argon / oxygen = 10 / 1 (pressure of 0.34Pa), the resistance heating vacuum evaporation of the SiO was carried out, the laminating of the middle resistance film was carried out by solid one by the thickness of 1 micrometer on the ITO electrode pattern, and the substrate with the middle resistance film was produced. The obtained film was transparent and amorphous at X diffraction measurement. Si / (In+Sn) surface ratio = About 25 atoms % and a volume resistivity are 7×10^3 . They were omega-cm and 5.5eV of ionization energy.

[0047] On the substrate with the middle resistance film produced in the <example 2> example 1, it is an electron hole transportation layer. N, N'-diphenyl-N, N'-(1-naphthyl)- After vapor-depositing [the benzidine] 50nm for aluminum oxine complex in order as 50nm and a luminous layer and carrying out 0.5nm vapor codeposition of the LiF as cathode, 200nm laminating of the aluminum was carried out, and 18 elements were produced for the organic LED component (light-emitting part 2x3mm²) on the substrate. In addition, the component was produced all over the clean booth of a class 1000.

[0048] All the 18 elements that produced this component measured resistance between terminals including wiring resistance with the circuit tester (about 1.7V impression), and there was no short circuit with the resistance more than 30 M omega (upper limit of circuit tester measurement). All components are 5000-hour or more 500 cd/m² at the electrical potential difference not more than 7V. Light is emitted to stability by the above brightness.

[0049] The component was produced like the example 2 using the ITO substrate (4.8eV of surface ionization energy) without the <example 1 of comparison> middle resistance film.

[0050] Consequently, during 18-piece production, 15 elements were measured with the circuit tester (about 1.7V impression), there is a component one element and whose 200Kohm 30 M omega or more and 11 M omega are one element and 1 Kohm, and the short-circuited component produced them. The component with 30-M omega or more resistance emits light to stability by the driver voltage not more than 7V for 5000 hours or more, within 1000 hours, the point emitting [un-] light would carry out breadth short-circuit, and the component not more than 200Kohm will not shine. The current potential property was formed into 1-2V high voltage rather than the component produced in the example 2.

[0051] <Example 3> It is RF magnetron sputtering (TOKUDA CFS-10EP-70) first. Taper etching (18 components of 2x3mm of light-emitting parts) of the distance of an ITO target (tin oxide 10wt%) with a diameter of 5 inches and a jig side was carried out to the shape of a stripe by the organic acid after room temperature membrane formation in 17.5cm and an argon ambient atmosphere (pressure of 0.34Pa) RF

output 300W, it annealed among 1-hour air at 300 degrees C, and the substrate with an ITO electrode pattern (20ohm/ **) (5cm angle) of 190nm of thickness was produced.

[0052] Next, carrying out the spatter of the indium oxide to a 3 inch RF magnetron SUPPATA ring gun by RF output 250 W using vacuum membrane formation equipment with the source of resistance heating vacuum evaporation by the argon / oxygen = 10 / 1 (pressure of 0.34Pa), the resistance heating vacuum evaporation of the SiO was carried out, and the laminating of the middle resistance film was carried out to coincidence by solid one by the thickness of 1 micrometer on the ITO electrode pattern. Then, it heat-treated at 300 degrees C among air, and the substrate with the middle resistance film was produced. The obtained film was transparent and amorphous at X diffraction measurement. Surface Si/In ratio = About 125 atoms % and a volume resistivity were 100 ohm-cm and 5.6eV of ionization energy.

[0053] 18 elements were produced like the example 2 on the substrate with the middle resistance film obtained in the <example 4> example 3.

[0054] Consequently, as for this component, the short circuit did not have 18 pieces with the resistance more than 30 M omega (it measures by 3V). All components are 5000-hour or more 500 cd/m2. Light is emitted to stability by the above brightness.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the explanatory view showing one example of the substrate with the middle resistance film of this invention.

[Drawing 2] It is the explanatory view showing one example of the substrate with the middle resistance film of this invention.

[Drawing 3] It is the explanatory view showing the conventional example.

[Drawing 4] It is the explanatory view showing one example of the substrate with the middle resistance film of this invention.

[Description of Notations]

- 1 ... Substrate
- 2 ... Electrode
- 3 ... Middle resistance film
- 4 ... Organic luminescence medium
- 5 ... Foreign matter

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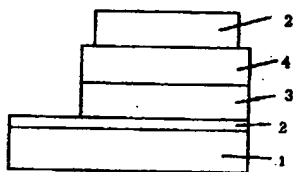
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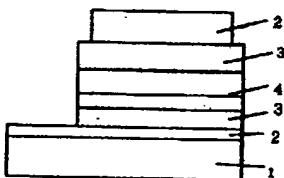
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DRAWINGS

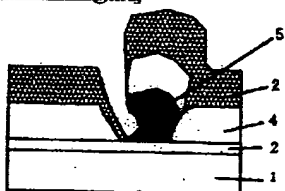
[Drawing 1]



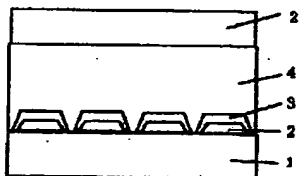
[Drawing 2]



[Drawing 3]



[Drawing 4]



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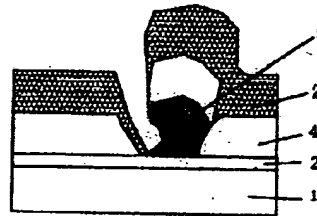
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(54)【発明の名称】 有機LED素子用中間抵抗膜付基板および有機LED素子

(57)【要約】

【課題】短絡を抑制する有機LED素子用基板および信頼性の高い有機LED素子を提供する。

【解決手段】ガラスまたは樹脂からなる透明基板1上に形成された透光性電極パターンからなる陽極または陰極2上の発光領域上の一部または全ての上を膜厚10nm～10μm、かつ、1cm²当たりの膜厚方向の電気抵抗が0.01～2Ω、かつ抵抗膜表面のイオン化エネルギーが5.1eV以上の透光性金属酸化物からなる中間抵抗膜3を積層することにより、電極表面の突起や付着した異物5の陰になり蒸着膜に欠陥が生じても短絡を防止し素子の欠陥拡大を防止する。



【特許請求の範囲】

【請求項1】 ガラスまたは樹脂からなる透明基板上に形成された透光性電極パターンからなる陽極または陰極上の発光領域上の一部または全ての上を膜厚10nm～10μm、かつ、1cm²当たりの膜厚方向の電気抵抗が0.01～2Ω、かつ抵抗膜表面のイオン化エネルギーが5.1eV以上の透光性金属酸化物からなる中間抵抗膜が積層されたことを特徴とする有機LED素子用中間抵抗膜付基板。

【請求項2】 中間抵抗膜が少なくとも導電性金属酸化物として酸化亜鉛で成膜または焼成されたインジウム酸化物からなることを特徴とする請求項1の有機LED素子用基板。

【請求項3】 中間抵抗膜が少なくとも導電性金属酸化物と非導電性金属酸化物との複合酸化物膜、または少なくとも導電性金属酸化物と非導電性金属窒化物との複合酸化物膜であることを特徴とする請求項1の有機LED素子用基板。

【請求項4】 導電性金属酸化物としてインジウム酸化物、非導電性金属酸化物としてケイ素酸化物を含む複合酸化物膜であることを特徴とする請求項2の有機LED素子用基板。

【請求項5】 請求項1～4の有機LED素子用中間抵抗膜付基板の発光領域上の一部または全ての上に少なくとも有機発光媒体層、対向電極層を順に積層し形成したことを特徴とする有機LED素子。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は有機発光ダイオード(LED)素子に係わる。

【0002】

【従来の技術】 通常、有機LED素子は、ガラス板や透明樹脂フィルム等の透明基板上に陽極パターン、有機発光媒体層、陰極金属層の順に形成される。陽極としてはITO（インジウムと錫の複合酸化物）、IZO（インジウムと亜鉛の複合酸化物）等の透明酸化物膜、または膜厚10nm以下で透光性の金、パラジウム、白金、銅等の単体金属膜、またはそれらの合金膜、または透明酸化物電極と金属膜の積層膜、または、発光領域における開口率が50%以上のスリット状またはメッシュ状金属電極、ポリチオフェン系導電性ポリマーの塗布電極等が使用される。

【0003】 次に、陽極上に有機正孔輸送層、有機発光層、有機電子注入層等からなる厚さ100～150nm程度の有機発光媒体層が蒸着、湿式コーティング等の方法で形成された後、陰極としてMgAg合金、AlLi合金、Al等の陰極が蒸着され有機LED素子が形成される。

【0004】 また、陰極はMgAg合金等を10nm以下の透光性に形成した後ITO、IZO等の透明導電性

酸化物膜を形成することにより、透明な有機LED素子を作製することも可能である。

【0005】 より低電圧で高輝度を得るため、界面のイオン化エネルギーを低下させ電子注入効率を向上するため有機発光媒体層と陰極層間にLi結体、LiF、酸化LiやCsのアルカリ金属含有層を形成することも行われている。

【0006】 また、有機LED素子は通常とは逆に透明基板上に陰極、有機発光媒体、陽極の順に形成することも可能である。

【0007】 有機LED素子の作製上の問題点としては、基板1上の陽極、陰極電極2間の有機発光媒体4層が非常に薄いため、陽極表面に微小な突起や付着異物5がある場合、図3で示すようにその陰の部分には有機発光媒体が蒸着されず、陰極金属が蒸着された際にその部分で陽極と陰極が直接接触したり、陽極陰極間に空洞が生じたりすることにより、リーク電流や放電を起こし素子を破壊する原因となる問題がある。

【0008】 破壊部で発生したガスは陰極金属層を持ち上げ、発光層または電子注入層から陰極を剥離させるとともに、陰極に開いた穴から水分、酸素が侵入し陰極の酸化を引き起こすため、破壊部を中心とした非発光点が生じる。

【0009】 そのため、陽極は数10nm以上の突起が無いことが望まれる。ITO膜は、通常、低抵抗化のため200℃以上で高温スパッタし成膜しているが、結晶粒が成長し表面が数10nmの凸凹になる。凸凹は研磨による表面平滑化が試みられたが研磨傷や研磨剤が残りやすく、うねりのあるガラス板上の薄膜を均一な厚さに研磨するためにはクラスターイオンビーム等による特殊な研磨法が必要であった。

【0010】 また、高温成膜したITOを酸でウエットエッチングしパターン形成する場合には膜が多結晶のため結晶粒の影響でエッチング端が凸凹になり、その陰により有機発光媒体蒸着層が薄くなったり、突起部に高電界がかかり素子が短絡しやすい問題もあった。

【0011】 成膜時点で平滑にする方法としては、基板温度を室温程度以下で成膜したアモルファス膜を用いる方法がある。アモルファス膜は極めて表面平滑性が高く、エッチング端をテーパー状に形成できるためアモルファスITO膜やIZO膜は、リーク電流や短絡を減らすのに効果を上げているが、抵抗率が高温成膜したITOの1.5倍程度高い問題と付着異物による短絡の解決の方法にはなっていない。

【0012】 基板上への付着異物を防ぐためにはクリーンルームで基板を扱うが、0.1μm程度のほこりを大面積基板上に一つも付着させないことは極めて困難な問題であった。

【0013】 基板上に付着異物があっても短絡を防ぐ方法としては、正孔輸送層を蒸着後ガラス転移温度以上に

加熱処理し軟化流動させ、付着異物の陰になり未蒸着になった部分を埋めることも可能だが、通常使われている正孔輸送層材料は加熱により結晶化し膜が凹凸になりやすく、そのため、加熱により結晶化せずアモルファス性の非常に高い特殊な分子構造を持つ高価な正孔輸送材料が必要になることと、加熱冷却に時間がかかり生産性に問題があった。

【0014】

【発明が解決しようとする課題】本発明は以上の問題点を鑑みて成されたものであり、有機LED素子の電極表面の突起や基板付着異物によるリーク電流や電氣的短絡の悪影響を抑制することを目的とする。

【0015】

【課題を解決するための手段】すなわち本発明は、ガラスまたは樹脂からなる透明基板上に形成された透光性電極パターンからなる陽極または陰極上の発光領域上の一部または全ての上を膜厚10nm～10μm、かつ、1cm²当たりの膜厚方向の電気抵抗が0.01～2Ω、かつ抵抗膜表面のイオン化エネルギーが5.1eV以上の透光性金属酸化物からなる中間抵抗膜が積層されたことを特徴とする有機LED素子用中間抵抗膜付基板である。また、中間抵抗膜が少なくとも導電性金属酸化物として酸化亜鉛で成膜または焼成されたインジウム酸化物からなることを特徴とする請求項1の有機LED素子用基板である。また、中間抵抗膜が少なくとも導電性金属酸化物と非導電性金属酸化物との複合酸化物膜、または少なくとも導電性金属酸化物と非導電性金属窒化物との複合酸化窒化物膜であることを特徴とする請求項1の有機LED素子用基板である。また、導電性金属酸化物としてインジウム酸化物、非導電性金属酸化物としてケイ素酸化物を含む複合酸化物膜であることを特徴とする請求項2の有機LED素子用基板である。

【0016】更に、本発明は上記基板上に少なくとも有機発光媒体層と対向電極層を順に積層した有機LED素子である。

【0017】

【発明の実施の形態】本発明では、低抵抗率な透明電極と高抵抗率な有機発光媒体4膜の中間の抵抗を有する中間抵抗膜3が、有機LED素子用の基板1上に形成された陽極または陰極からなる電極2パターンに接し、かつ発光領域の一部または全てを覆い1層の膜が配置される(図1参照)。または、基板上に形成された陽極または陰極パターンと、対極のそれぞれに接し、かつ発光領域の一部または全てを覆い2層の膜が配置されることも可能である(図2参照)。

【0018】以下に本発明についてさらに詳しく説明する。通常陰極に用いられているAl等の金属電極の体積抵抗率は10⁻⁵Ω・cm以下であり、ITO等の透明電極の体積抵抗率は2×10⁻⁴Ω・cm以下である。

【0019】発光媒体層の抵抗は、発光媒体層が50nm

mのトリフェニルアミン系正孔輸送層、50nmのAlオキシシラン錯体発光層からなる一般的な有機LED素子の例では、有機発光媒体は非線形な抵抗を示し、印加電圧が高いほど抵抗が低くなる。例えば通常有機LEDは10V以内の駆動電圧で駆動するが、その場合、無欠陥な有機発光媒体層の体積抵抗率は最高駆動電圧の10Vで約10⁶Ω・cmであり、他の有機LED用発光媒体材料を用いた場合でも概略10⁶Ω・cmの抵抗率である。

【0020】その場合、発光媒体層の膜厚方向の抵抗は1cm²当たり10Ωとなる。そこで、体積抵抗率10⁻⁵Ω・cmの電極材料が0.1μm角の面積(10⁻¹⁰cm²)で0.1μmの長さで電極間を短絡し欠陥を生じさせたとすると、欠陥箇所の抵抗は1カ所当たり1Ωであり、欠陥密度が1箇所/cm²の場合、電極間の抵抗は1cm²当たり約0.9Ωとなる。

【0021】その結果、面積1cm²の定電流駆動素子の場合には1カ所欠陥があると欠陥部で電流の大部分が半分リークし印加電圧が減少するとともに輝度が激減してしまう問題があった。また、定電圧駆動素子の場合には欠陥部の電流密度が高くなり、ジュール熱により素子の破壊につながる問題があった。

【0022】また、XYマトリクスディスプレイの場合は、欠陥部からのリーク電流でクロストークが増大し、表示が不鮮明になる問題があった。

【0023】本発明の中間抵抗膜は、基板表面の異物付着や突起等による有機発光媒体の蒸着不良欠陥カ所での電極同士の直接接触を防止し、有機発光媒体の蒸着不良カ所においては中間抵抗膜を通して電流がリークするためリーク電流は電極同士が直接接触した場合に比べて大幅に抑制できる。

【0024】中間抵抗膜の抵抗は、発光媒体の抵抗と直列にかかるため、電力損失を小さくするために発光媒体の膜厚方向の抵抗値の1/5以下が望ましい。すなわち10V以下の駆動電圧で駆動する場合、発光媒体の抵抗が最低な10V印加時に中間抵抗膜無しの有機LED素子の抵抗が1cm²当たり10Ωであるとする、中間抵抗膜の膜厚方向の抵抗は2Ω以下、好ましくは0.5Ω以下とすることで、中間抵抗膜を入れた場合の抵抗増加による有機LED素子の電流-電圧特性の悪化を抑制できる。

【0025】膜厚方向の抵抗膜の抵抗値が発光媒体の膜厚方向の抵抗の1/5以上の場合、素子の駆動電圧は、配線抵抗を無視すると1.2倍以上上昇し発光効率が低下するとともに、抵抗層でのジュール熱の増加により素子の劣化が速まる。

【0026】また、XYマトリクスディスプレイの透明電極ラインを形成した基板上に本発明の中間抵抗膜をベタで積層する場合は、膜厚方向の中間抵抗膜の抵抗値が発光媒体の膜厚方向の抵抗値の1/1000以下で透明

電極ライン間のスペースが数 μm 以下に狭い場合、透明電極間のリーク電流が無視できなくなり、クロストークが生じる場合がある。

【0027】その場合は、中間抵抗膜3の抵抗が低い場合は膜厚を薄めにするか、または図4のように透明電極ラインごとに分離して積層することが望ましい。

【0028】本発明の有機LED素子用基板の中間抵抗膜の厚さは、 $10\text{nm}\sim 10\mu\text{m}$ の厚さで形成される。中間抵抗膜の厚さが発光媒体層と同じ 100nm 程度の場合は体積抵抗率 $10^4\sim 10^5\Omega\cdot\text{cm}$ 程度の抵抗膜を用いることが望ましい。

【0029】中間抵抗膜を 10nm 以下にした場合は、電極表面の凹凸や付着異物を十分にカバーできない場合がある。

【0030】中間抵抗膜を $10\mu\text{m}$ 以上に形成した場合は、膜応力による膜剥がれや割れの問題、成膜コストが増す問題、陽極電極間または選択していない陽極と陰極間でのリーク電流が増して発光のにじみやクロストークが生じ易い。

【0031】中間抵抗膜を透光性陽極上に積層し、陽極側から光を取り出す場合には中間抵抗膜も有機LEDの発光スペクトルをできるだけ透過することが望ましい。本発明ではエネルギーギャップが広く可視光領域で50%以上光透過可能な材料として金属酸化物材料を用いる。

【0032】中間抵抗膜に使用する金属酸化物材料としては透明導電膜材料として知られている材料の抵抗率を高めて用いることができる。

【0033】透明導電膜材料として知られている材料の例としては、 Mg 、 Zn 、 Ga 、 Ge 、 In 、 Sn から少なくとも一つ以上選ばれた金属の酸素欠損型透明導電性酸化物または複合酸化物が上げられる。具体的には In_2O_3 、 $\text{In}_{2-x}\text{Ga}_x\text{O}_3$ 、 ITO 、 IZO 、 SnO_2 、 $\text{Sn}_{1-x}\text{Ge}_x\text{O}_2$ 、 ZnO 、 $\text{Zn}_x\text{Mg}_{1-x}\text{O}$ 、 AgInO_2 等がある。

【0034】また、 Sr 、 Ni 、 Cu 、 Al から少なくとも一つ以上選ばれた金属の酸素過剰型透明導電性金属酸化物または複合酸化物が上げられる。具体的には NiO 、 CuAlO_2 、 SrCu_2O_2 等がある。

【0035】これらの膜の抵抗率を高める方法としては、酸素欠損型透明導電性金属酸化物または複合酸化物の場合は、通常低抵抗な酸化物膜を反応性蒸着やスパッタで成膜する条件よりも成膜雰囲気中の酸素濃度を高めて成膜し膜中の酸素欠損を減らすか、または成膜後、酸化雰囲気中で熱処理することにより酸素欠損を減らしキャリア密度を減らすことである。または、酸素欠陥をつぶす Li 、 Cu 等の1価金属をドーピングすることによっても導電性を低下させ適当な抵抗値に高めることができる。

【0036】酸素過剰型透明導電性金属酸化物または複合酸化物の場合は、逆に通常低抵抗な酸化物膜を成膜す

る条件よりも成膜時の酸素濃度を減らすか、成膜後還元雰囲気中で焼成することである。

【0037】 In を含む酸素過剰型透明導電性金属酸化物または複合酸化物の場合は、成膜時には膜が金属膜または不完全な金属酸化物であってもよく、成膜後に酸素やオゾン雰囲気等の酸化雰囲気中で $150^\circ\text{C}\sim 400^\circ\text{C}$ で処理し酸化を進行させ酸化物膜を形成することもできる。しかし、熱処理は中間抵抗膜の結晶化を進行させ、結晶化に伴う移動度向上により所望の抵抗値よりも低抵抗化してしまう場合もある。

【0038】また、他の抵抗率を高める方法としては、導電性金属酸化物中に抵抗率が高い SiO_2 、 Al_2O_3 、 GeO_2 、 Ta_2O_5 、 Y_2O_3 等の非導電性金属酸化物または Si_3N_4 等の非導電性金属窒化物を（非導電性金属酸化物または窒化物中の金属原子数）／（導電性金属酸化物中の金属原子数）比で $1/10\sim 10/1$ 程度の適当な割合で混合し複合することである。

【0039】導電性金属酸化物と非導電性金属酸化物または窒化物を複合させる方法は、それらの構成金属または金属酸化物及び金属窒化物を予め複合した蒸発材料またはターゲット材料を用いるか、または別々の蒸発源またはターゲットより同時に、酸素および窒素雰囲気下反応性蒸着、パルスレーザー堆積、スパッタ法等を行い成膜できる。

【0040】具体的には、非導電性金属酸化物であるシリカ等のケイ素酸化物、アルミナ等のアルミ酸化物または非導電性金属窒化物であるケイ素窒化物を導電性金属酸化物である酸化 In や ITO のターゲット中に予め混合しスパッタする。または、 In を酸素雰囲気中で反応性蒸着しながら同時に SiO を共蒸着する。または、 In と SiO を共蒸着した後酸素雰囲気中で焼成する等の方法で中間抵抗膜を作製できる。

【0041】例えば酸素雰囲気中で酸化 In をスパッタ中に金属原子比 $10\sim 200\%$ 程度の割合で SiO を共蒸着し基板温度室温で成膜すると、平滑なアモルファス性の高い膜が形成でき、 300°C 程度に加熱した場合でも膜中の非導電性ケイ素酸化物が導電性の酸化 In の結晶化を妨げ、結晶化に伴う移動度向上による低抵抗化を抑制することができ熱安定性が高まる。

【0042】また、中間抵抗膜付き有機LED素子用基板においては、中間抵抗膜は有機発光媒体層に正孔を注入しやすくするために、その表面は有機発光媒体を構成する正孔輸送材料と同等の大きなイオン化エネルギーを持つ必要がある。

【0043】一般的に有機LEDに用いられている銅フタロシアニンやトリフェニルアミン系正孔輸送材料は理研計器製表面分析装置AC-1で測定し $5.1\sim 5.8\text{eV}$ 、発光材料の Al オキシニル錯体は 5.8eV 程度のイオン化エネルギーを持つため、低駆動電圧で効率良く正孔輸送層または発光層の有機発光媒体に正孔注入する

ためには少なくとも5.1 eV以上、好ましくは5.8 eV程度のイオン化エネルギーが求められる。

【0044】本発明では透明酸化物導電膜とケイ素酸化物をケイ素以外の金属原子に対して10~200原子%程度複合化することによりキャリア密度も下がるため通常低抵抗な透明電極として用いられているITOの4.8 eVより大きな5.5 eV以上のイオン化エネルギーを実現することもできる。

【0045】

【実施例】<実施例1>まず、RFマグネトロンスパッタリング(TOKUDA CFS-10EP-70)により直径5インチのITOターゲット(酸化錫10wt%)とジグ面との距離を17.5 cm、アルゴン雰囲気(圧力0.34 Pa)でRF出力300 Wで室温成膜後、ストライプ状に有機酸でテーパーエッチング(発光部2×3 mmの素子18素子分)した。次に300℃で1時間空気中アニールし膜厚190 nmのITO電極パターン(20 Ω/□)付基板(5センチ角)を作製した。

【0046】次に、3インチRFマグネトロンスパッタリングガンと抵抗加熱蒸着源付き真空成膜装置を用い、アルゴン/酸素=10/1(圧力0.34 Pa)でRF出力250 WでITOをスパッタしながらSiOを抵抗加熱蒸着しITO電極パターン上に中間抵抗膜を1 μmの厚さでベタで積層し中間抵抗膜付き基板を作製した。得られた膜は透明で、X線回折測定でアモルファスであった。表面のSi/(1n+Sn)比=約25原子%、体積抵抗率は $7 \times 10^3 \Omega \cdot \text{cm}$ 、イオン化エネルギー5.5 eVであった。

【0047】<実施例2>実施例1で作製した中間抵抗膜付基板上に、正孔輸送層としてN,N'-ジフェニル-N,N'-(1-ナフチル)-ベンジジン(50 nm、発光層としてAlオキシシメタンを50 nmを順に蒸着し、陰極としてLiFを0.5 nm共蒸着した後、Alを200 nm積層し有機LED素子(発光部2×3 mm²)を基板上に18素子を作製した。なお、素子はクラス1000のクリーンブース中で作製した。

【0048】この素子は作製したすべての18素子は、配線抵抗を含む端子間の抵抗をテスターで測定(約1.7 V印加)し、30 MΩ(テスター測定の上限)以上の抵抗を持ち短絡はなかった。素子はすべて7 V以下の電圧で5000時間以上500 cd/m²以上の輝度で安定に発光する。

【0049】<比較例1>中間抵抗膜無しのITO基板(表面のイオン化エネルギー4.8 eV)を用いて実施例2と同様に素子を作製した。

【0050】その結果、18個作製中15素子は、テスターで測定(約1.7 V印加)し、30 MΩ以上、11 MΩが1素子、200 KΩが1素子、1 KΩの素子が1素子で、短絡した素子が生じた。30 MΩ以上抵抗のあ

る素子は7 V以下の駆動電圧で5000時間以上安定に発光し、200 KΩ以下の素子は1000時間以内に非発光点が広がりショートし光らなくなった。電流電圧特性は実施例2で作製した素子よりも1~2 V高電圧化した。

【0051】<実施例3>まず、RFマグネトロンスパッタリング(TOKUDA CFS-10EP-70)により直径5インチのITOターゲット(酸化錫10wt%)とジグ面との距離を17.5 cm、アルゴン雰囲気(圧力0.34 Pa)でRF出力300 Wで室温成膜後、ストライプ状に有機酸でテーパーエッチング(発光部2×3 mmの素子18素子分)し、300℃で1時間空気中アニールし膜厚190 nmのITO電極パターン(20 Ω/□)付基板(5センチ角)を作製した。

【0052】次に、3インチRFマグネトロンスパッタリングガンと抵抗加熱蒸着源付き真空成膜装置を用い、アルゴン/酸素=10/1(圧力0.34 Pa)でRF出力250 Wで酸化インジウムをスパッタしながら同時にSiOを抵抗加熱蒸着しITO電極パターン上に中間抵抗膜を1 μmの厚さでベタで積層した。その後、空気中300℃で熱処理し中間抵抗膜付き基板を作製した。得られた膜は透明で、X線回折測定でアモルファスであった。表面のSi/In比=約125原子%、体積抵抗率は100 Ω·cm、イオン化エネルギー5.6 eVであった。

【0053】<実施例4>実施例3で得られた中間抵抗膜付基板上に実施例2と同様に18素子作製した。

【0054】その結果、この素子は18個が30 MΩ(3 Vで測定)以上の抵抗を持ち短絡はなかった。素子はすべて5000時間以上500 cd/m²以上の輝度で安定に発光する。

【0055】

【発明の効果】以上により明らかなように、本発明による中間抵抗膜付基板は、有機LED素子の電極表面の突起や基板付着異物によるリーク電流や電氣的短絡の悪影響を抑制することができる。従って、有機LED素子とした場合には、欠陥拡大防止と長寿命化に効果がある。

【0056】

【図面の簡単な説明】

【図1】本発明の中間抵抗膜付基板の一実施例を示す説明図である。

【図2】本発明の中間抵抗膜付基板の一実施例を示す説明図である。

【図3】従来例を示す説明図である。

【図4】本発明の中間抵抗膜付基板の一実施例を示す説明図である。

【符号の説明】

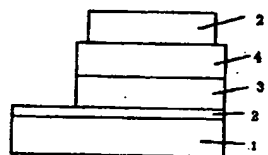
1... 基板
2... 電極
3... 中間抵抗膜

4...有機発光媒体

5...異物

【図1】

【図2】



【図3】

【図4】

